

COSMETIC COMPOSITION CONTAINING AT LEAST ONE TACKY POLYMER AND AT  
LEAST ONE SETTING POLYMER

Isabelle Rollaty-Corvol and Henri Samain

INTERNATIONAL PATENT OFFICE  
WORLD ORGANIZATION FOR INTELLECTUAL PROPERTY

International patent published on  
the basis of the Patent Cooperation Treaty  
INTERNATIONAL PUBLICATION NO. WO 99/63955

International Patent Classification <sup>6</sup> :	A 61 K 7/06
International Filing No.:	PCT/FR99/01347
International Filing Date:	June 8, 1999
International Publication Date:	December 16, 1999
Priority	
Date:	June 11, 1998
Country:	FR
No.:	98/07376

COSMETIC COMPOSITION CONTAINING AT LEAST ONE TACKY POLYMER AND AT  
LEAST ONE SETTING POLYMER

[Composition cosmétique comprenant au moins un polymère collant et au moins un polymère  
fixant]

Inventors; and Inventor/Applicants (only for US):	Isabelle Rollaty-Corvol and Henri Samain
--	---

Applicant (for all designated states except US):	L'Oreal
---	---------

Designated States:	AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO Patent
--------------------	---

(GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG)

Published:

With international search report.

Before expiration of the time period provided for modification of the claims, will be re-published if modifications are received.

## FOR INFORMATION ONLY

Codes for the identification of PCT contract states on the cover sheets of the documents that publish the international applications in accordance with the PCT.

AL	Albania	KE	Kenya	SZ	Swaziland
AM	Armenia	KG	Kyrgyzstan	TD	Chad
AT	Austria	KP	Democratic	TG	Togo
AU	Australia		People's Republic	TJ	Tajikistan
AZ	Azerbaijan		of Korea	TM	Turkmenistan
BA	Bosnia- Herzegovina	KR	Republic of Korea	TR	Turkey
BB	Barbados	KZ	Kazakhstan	TT	Trinidad and Tobago
BE	Belgium	LC	Saint Lucia	UA	Ukraine
BF	Burkina Faso	LI	Liechtenstein	UG	Uganda
BG	Bulgaria	LK	Sri Lanka	US	United States of America
BJ	Benin	LR	Liberia	UZ	Uzbekistan
BR	Brazil	LS	Lesotho	VN	Vietnam
BY	Belarus	LT	Lithuania	YU	Yugoslavia
CA	Canada	LU	Luxembourg	ZW	Zimbabwe
CF	Central African Republic	LV	Latvia		
CG	Congo	MC	Monaco		
CH	Switzerland	MD	Republic of Moldavia		
CI	Côte d'Ivoire	MG	Madagascar		
CM	Cameroon	MK	Macedonia (former Yugoslavian Republic of Macedonia)		
CN	China				
CU	Cuba	ML	Mali		
CZ	Czech Republic	MN	Mongolia		
DE	Germany	MR	Mauritania		
DK	Denmark	MW	Malawi		
EE	Estonia	MX	Mexico		
ES	Spain	NE	Niger		
FI	Finland	NL	Netherlands		
FR	France	NO	Norway		
GA	Gabon	NZ	New Zealand		
GB	United Kingdom	PL	Poland		
GE	Georgia	PT	Portugal		
GH	Ghana	RO	Romania		
GN	Guinea	RU	Russian Federation		
GR	Greece	SD	Sudan		
HU	Hungary	SE	Sweden		
IE	Ireland	SG	Singapore		
IL	Israel	SI	Slovenia		
IS	Iceland	SK	Slovakia		
IT	Italy	SN	Senegal		
JP	Japan				

The invention relates to a cosmetic composition for keratinic fibers such as hair, which contains, in a cosmetically acceptable medium, at least one tacky polymer with a vitreous transition temperature less than 20°C and at least one setting polymer with a vitreous transition temperature greater than 15°C. It also relates to a process for treatment of keratinic fibers such as the hair, and in particular to a process for setting and/or maintaining of the hair style implementing said composition, as well as to the use of this composition in or for the manufacturing of a cosmetic hair styling formulation.

In the sense of the present invention, "keratinic fibers" are understood to mean hair, eye lashes and eye brows, and "tacky polymer" is understood to mean a polymer which, after application by pressure onto an identical polymer, resists an attempt at separation.

Setting of the hair style is an important hair styling element which consists of maintaining the shape already produced or of shaping the hair and setting it simultaneously. "Setting polymer" is understood to mean a polymer which maintains the hair in their shape or which enables one to shape the hair and set it simultaneously.

The most widespread hair products for shaping and/or maintaining of the hair style on the cosmetic market are spray compositions essentially consisting of a solution, most often alcoholic or aqueous, and one or more materials, generally polymer resins, whose function is to form bonds between the hairs, also called setting materials, in a mixture with various cosmetic additives. This solution is generally packaged in an appropriate aerosol container pressurized by means of a propellant, or in a pump bottle.

Hair styling gels or foams are also known, which are generally applied on wet hair before brushing or setting. Unlike the conventional aerosol lacquers, these compositions have the disadvantage of not allowing setting of hair which is in an already produced shape. In effect, these compositions are essentially aqueous, and their application moistens the hair and therefore cannot maintain the initial shape of the hair style. In order to shape and set the hair style, one must therefore then brush or dry it.

The majority of the compositions of the state of the art have the same disadvantage of not setting the hair in a sufficiently lasting manner. Thus, the shape initially given to the hair style gradually becomes less distinct in the course of the day, and this occurs all the more quickly if the person is in motion. Consequently, it is often necessary to begin all the styling and setting operations again if one wishes to regain the initial hair style.

Hair styling compositions are therefore sought, which provide sufficiently strong setting and maintaining effect so that the hair style suitably resists the different forces over time.

---

\* [Editor's note: Numbers in the right margin represent pagination of the original foreign language text.]

Finally, the compositions intended for setting the hair style sometimes have the disadvantage of altering the cosmetic properties of the hair. Thus, the hair can become rough, difficult to untangle, lose its pleasant feel and appearance. Hair styling compositions which provide suitable cosmetic properties are therefore sought particularly in terms of untangling, softness, and feel.

There is therefore a need to find cosmetic compositions, particularly for hair styling, which do not have the group of disadvantages indicated above.

In a surprising and unexpected manner, the Applicant has discovered that when tacky polymers, in particular branched sulfonic polyesters or (meth)-acrylic ester polymers, are associated with setting polymers, it is possible to obtain cosmetic compositions which meet the needs expressed above. /3

The invention therefore relates to a cosmetic composition for keratinic fibers such as the hair, which contains, in a cosmetically acceptable medium, at least one tacky polymer with a vitreous transition temperature ( $T_g$ ) less than  $20^\circ\text{C}$  and at least one setting polymer with a vitreous transition temperature ( $T_g$ ) greater than  $15^\circ\text{C}$ .

Advantageously, a tacky polymer having a detachment profile defined by a maximum detachment force of at least  $F_{\max} > 3$  Newton and preferably greater than 5 N is chosen.

Even more advantageously, the detachment profile is moreover defined by a separation energy  $\dot{S}_{s(M/V)}$  of the material put in contact with a glass surface, which is less than  $300 \mu\text{J}$ , when the vitreous transition temperature of the tacky polymer is less than  $-15^\circ\text{C}$ .

The maximum detachment force  $F_{\max}$  is the maximum tensile force, measured using an extensometer, necessary to detach the respective  $38 \text{ mm}^2$  surfaces of two rigid, inert, non-absorbent supports (A) and (B) placed facing one another; said surfaces being coated beforehand with the tacky polymer dissolved beforehand at a concentration of 5% in an aqueous, hydroalcoholic or alcoholic solvent, in a proportion of  $1 \text{ mg/mm}^2$ , dried for 24 h at  $22^\circ\text{C}$  in a relative humidity of 50%, and then subjected for 20 sec to a compression of 3 Newton, and finally subjected for 30 sec to traction at a speed of 20 mm/minute.

Supports (A) and (B) consisting of polyethylene, polypropylene, metallic alloy or glass are advantageously used. /4

The separation energy  $S_{s(M/V)}$  is the energy provided by the extensometer in order to separate the respective  $38 \text{ mm}^2$  surfaces of two rigid, inert, non-absorbent supports (C) and (D) placed facing one another; one of said supports consists of polished glass, and the nature of the other of said supports is identical to that of supports (A) and (B) as defined in Claim 2 or 3 and whose surface is coated beforehand with the tacky polymer dissolved beforehand at a concentration of 5% in an aqueous, hydroalcoholic or alcoholic solvent, in a proportion of  $1 \text{ mg/mm}^2$ , dried for 24 h at  $22^\circ\text{C}$  in a relative humidity of 50%, the two surfaces of said

supports (C) and (D) being subjected for 20 sec to a compression of 3 Newton, and finally subjected for 30 sec to traction at a speed of 20 mm/minute.

The separation energy  $S_{s(M/V)}$  is work which can be computed by means of the following formula:

$$\int_{x_{s1} + 0,05}^{x_{s2}} F(x) dx$$

in which  $F(x)$  is the force necessary to produce a movement (x);

$x_{s1}$  is the movement (expressed in millimeters) produced by the maximum tensile force;

$x_{s2}$  in which [sic; is] the movement (expressed in millimeters) produced by the tensile force allowing complete separation of the two surfaces of supports (C) and (D).

Preferably, a tacky polymer will be chosen such that the maximum detachment force  $F_{max}$  is greater than 5 Newton and/or such that its temperature of vitreous transition ( $T_g$ ) is less than 20°C. If the  $T_g$  of the polymer is less than -15°C, it should preferably moreover have a separation energy  $S_{s(M/V)}$  less than 300  $\mu J$ .

The relative concentration by weight of tacky polymer in the composition is generally greater than 0.01%, and more preferably greater than 0.1%, and even more preferably greater than 0.5%. /5

According to a first advantageous embodiment of the present invention, a branched sulfonic polymer or (meth)-acrylic ester polymer [or] polymers is (are) chosen as tacky polymer.

Advantageously, a setting polymer with a vitreous transition temperature ( $T_g$ ) greater than 25°C is chosen.

According to the invention, the relative concentration by weight of setting polymer in the composition is generally greater than 0.01% and preferably greater than 0.1%.

A particularly preferred from of the branched sulfonic polyester is that obtained by polymerization of:

- (i) at least one bifunctional dicarboxylic acid carrying no sulfonic function; /6
- (ii) at least one bifunctional monomer carrying at least one sulfonic function, the functional group(s) being chosen from the group which includes the hydroxyl, carboxyl and amino groups;
- (iii) at least one diol or mixture of diol(s) and diamine(s);
- (iv) possibly, a bifunctional monomer chosen from the group which includes the carboxylic hydroxyacids, the carboxylic aminoacids and their mixtures;
- (v) at least one multifunctional reagent carrying at least three functional groups chosen from the group which includes the amino, alcohol and carboxylic acid groups.

Such polymerization can be carried out using:

- (i) at least one bifunctional dicarboxylic acid carrying no sulfonic function;
- (ii) 2 to 15 relative mole % of bifunctional monomer carrying at least one sulfonic function;
- (iii) at least one diol or mixture of diol(s) and diamine(s);
- (iv) 0 to 40 relative mole % of the bifunctional monomer chosen from the group which includes the carboxylic hydroxyacids, the carboxylic aminoacids and their mixtures;
- (v) 0.1 to 40 relative mole % of the multifunctional reagent carrying at least three reactive functional groups.

The branched sulfonic polymers preferably contain substantially equal proportions, in number of equivalents, on one hand, of carboxylic acid functions, and on the other hand, of diol and/or diol and diamine functions.

The bifunctional dicarboxylic acid (i) is preferably chosen from the group which includes the aliphatic dicarboxylic acids, the alicyclic dicarboxylic acids, the aromatic dicarboxylic acids or a mixture of them, and more particularly, from the group which includes 1,4-cyclohexanedioic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, fumaric acid, maleic acid, 1,3-cyclohexanedioic acid, phthalic acid, terephthalic acid, and isophthalic acid or their mixtures.

The bifunctional monomer (ii) as defined above is preferably chosen from the group which includes the dicarboxylic acids, the dicarboxylic acid esters, the glycols and hydroxyacids each containing at least one sulfonate metal group.

The diol (iii) is preferably chosen from the group which includes the alkanediols and the polyalkylenediols, and more particularly, from the group which includes ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol and polypropylene glycol.

The diamine (iii) can be chosen from the group which includes the alkanediamines and the polyalkylenediamines.

The multifunctional reagent (v) is preferably chosen from the group which includes trimethylolethane, trimethylolpropane, glycerol, pentaerythritol, sorbitol, trimellitic anhydride, erythritol, threitol, dipentaerythritol, pyromellitic dianhydride and dimethylpropionic acid.

The branched sulfonic polymers referred to by the present invention are those described in the patent applications WO 95/181 91, WO 97/082 61 and WO 97/208 99.

According to the invention, the polymer AQ 1350 marketed by the company Eastman is advantageously chosen as branched sulfonic polymer. This polymer AQ 1350 is defined by:

- a vitreous transition temperature given by the supplier equal to 0°C;
- a maximum detachment force  $F_{max}$  equal to 25 N.

According to a second advantageous embodiment of the compositions according to the invention, a (meth)-acrylic ester polymer is used as tacky polymer.



The tacky (meth)-acrylic ester polymers used according to the invention advantageously include:

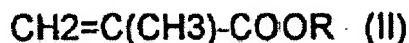
(a) 9 to 99 wt% of a (meth)-acrylic ester monomer with respect to the total weight of the polymer;

(b) up to 90% co-monomer(s);

(c) 1 to 10% of a vinylidene monomer containing a carboxyl or hydroxyl group.

/8

The (meth)-acrylic ester monomer (a) generally corresponds to formula (I) or (II):



in which R represents a  $\text{C}_1$  to  $\text{C}_{18}$  alkyl, a  $\text{C}_2$  to  $\text{C}_8$  alkoxyalkyl, a  $\text{C}_2$  to  $\text{C}_6$  alkylthioalkyl, or a  $\text{C}_2$  to  $\text{C}_8$  cyanoalkyl. For example, the monomer (a) can be chosen from the group which includes methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, hexyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methoxyacrylate, ethoxyacrylate, methylthiomethyl acrylate and cyanopropyl acrylate.

The co-monomer (b) can contain one or more vinylidene groups having terminal  $\text{CH}_2=\text{C}$  groups, such as:

- the acrylic or methacrylic esters, such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, methyl ethacrylate,
- the vinyl halides such as vinyl chloride;
- the vinyl and allyl esters such as vinyl acetate, vinyl butyrate, vinyl chloroacetate;
- the aromatic vinyls such as styrene, vinyltoluene, chloromethylstyrene, vinylnaphthalene; and
- the vinylic nitriles such as acrylonitrile or methacrylonitrile.

Among the vinylidene monomers (c) containing hydroxyl groups, it is possible to mention the acrylate monomers with terminal hydroxyl group, such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, hydroxybutyl acrylate, or else certain hydroxymethylated derivatives of acrylamide diacetone, for example, N-methylol acrylamide, N-methylol maleamide, N-propanolacrylamide, N-methylol methacrylamide, N-methylol-p-vinyl benzamide.

Among the vinylidene monomers (c) containing carboxyl groups, it is possible to mention, for example, acrylic or methacrylic acid, itaconic acid, citraconic acid, maleic acid.

The tacky (meth)-acrylic ester polymers referred to particularly by the present invention are those described in the patents US 5 234 627 and US 4 007 147.

According to the invention, the polymer Hycar 26 120 marketed by the company Goodrich is advantageously chosen as (meth)-acrylic ester polymer [or] polymers. This Hycar 26 120 polymer is defined by:

- a vitreous transition temperature given by the supplier equal to  $-10^{\circ}\text{C}$ ;
- a maximum detachment force  $F_{\text{max}}$  equal to 6.25 N.

The setting polymer is generally chosen from the anionic, cationic, amphoteric, non-ionic setting polymers and their mixtures.

These setting polymers can be used in solubilized form or else in the form of a dispersion of solid particles of polymer.

As cationic setting polymer, it is preferably to choose the polymers containing primary, secondary, tertiary and/or quaternary amine groups which are part of the polymer chain or directly connected to it, and having a molecular weight between 500 and approximately 5,000,000 and preferably between 1,000 and 3,000,000.

As anionic setting polymers, the polymer containing groups derived from carboxylic, sulfonic or phosphoric acid are preferable, and have a weight average molecular weight between 500 and 5,000,000.

As amphoteric setting polymers, it is preferable to choose the polymers containing units B and C statistically distributed in the polymer chain, in which B designates a unit derived from a monomer containing at least one basic function, in particular a basic nitrogen atom, and C designates a unit derived from an acidic monomer containing one or more carboxylic or sulfonic groups, or else B and C can designate groups derived from zwitterionic monomers of carboxybetaines or sulfobetaines; B and C can also designate a cationic polymer chain containing primary, secondary, tertiary or quaternary amine groups, in which at least one of the amine groups carries a carboxylic or sulfonic group connected by the intermediary of a hydrocarbon radical; or else B and C are part of a chain of a polymer with an ethylene  $\alpha,\beta$ -dicarboxylic unit of which one of the carboxylic groups was reacted with a polyamine containing one or more primary or secondary amine groups. /10

As non-ionic setting polymers, it is advantageous to choose the polyurethanes.

Among the setting polymers used in solubilized form, it will be preferable to use the polymers chosen from the group which includes the acrylic polymers containing silicone, the polymers based on vinyl pyrrolidone and vinyl caprolactam monomer.

Among the setting polymers present in the form of a dispersion, it will be preferable to use those containing acrylic or methacrylic monomers and their esters or else those containing styrene monomers.

The composition can be present in spray, foam, gel or lotion form, and the cosmetically acceptable vehicle can consist of an appropriate solvent, to which additives are added, such as gelling agents or foaming agents. In general, the solvent is chosen from water, the alcohols or a hydroalcoholic mixture.

/11

The compositions can moreover contain an appropriate quantity of propellant such as the usual compressed or liquefied gases, preferably compressed air, carbon dioxide or nitrogen, or a gas which is soluble or not in the composition, such as dimethyl ether, the hydrocarbons containing or not containing fluorine, and their mixtures.

The invention also relates to an aerosol device consisting of a vessel containing an aerosol composition made up, on one hand, of a liquid phase (or liquor) containing at least one composition according to the invention in an appropriate solvent and a propellant as well as a means for distribution of said aerosol composition.

Yet another object of the invention is a process for treatment of keratinic fibers, of the hair in particular, characterized by the fact that the composition according to the invention is applied on said fibers, before or after formation of the hair style.

The composition according to the invention is generally used in or for the manufacturing of a cosmetic hair styling formulation.

The examples hereafter make it possible to illustrate the invention but without seeking to limit its scope. The polymers indicated hereafter will be used.

Amphomer    Octylacrylamide/acrylate/butylaminoethyl/methacrylate copolymer marketed by National Starch

Polymer LO-21 DRY    Poly dimethyl/methyl siloxane with groups methyl propyl 3-thio acrylate groups/methyl methacrylate/methacrylic acid marketed by 3M

Luviskol VA64P    Polyvinylpyrrolidone marketed by BASF

/12

Uramul SC 132    Acrylic copolymer latex marketed by DMS RESINS; Tg = 50°C

AQ 1350    Branched sulfonic polyester marketed by the company Eastman

Examples:

Compositions according to the invention containing an association of a branched sulfonic polymer and a setting polymer are compared hereafter with compositions according to prior art containing either the branched sulfonic polymer alone or the setting polymer alone.

Example 1 (comparative)

Sensory tests were carried out in order to compare the performance of the compositions according to the invention and of compositions according to prior art. The comparison relates to the hair style holding power over time and under stress.

For this purpose, 3 compositions according to the invention and 4 compositions according to prior art are produced. These compositions are applied on wigs of natural hair. Then, the holding of the shape of the wig and the return of the shape of the wigs after agitation were evaluated.

Composition 1 (invention):

/13

AQ 1350	4 g
Amphomer	2 g
Water	75 g
2 amino-2-methyl-1-propanol qs neutralization of Amphomer	0.37 g
Alcohol qs	100 g

Composition 2 (invention):

AQ 1350	4 g
Polymer LO-21 DRY 90% neutralized beforehand	2 g
Water	75 g
Alcohol qs	100 g

Composition 3 (invention):

AQ 1350	4 g
Luviskol VA 64 P	2 g
Water	75 g
Alcohol qs	100 g

Composition 4 (prior art – branched sulfonic polyester alone):

AQ 1350	6 g
Water	75 g
Alcohol qs	100 g

Composition 5 (prior art – setting polymer alone):

Amphomer	6 g
Water	75 g
2 amino 2 methyl 1 propanol qs neutralization of Amphomer	1.09 g
Alcohol qs	100 g

Composition 6 (prior art – setting polymer alone):

Polymer LO-21 DRY 90% neutralized beforehand	6 g
Water	75 g
Alcohol qs	100 g

Composition 7 (prior art – setting polymer alone):

Luviskol VA 64 P	6 g
Water	75 g
Alcohol qs	100 g

Each of the compositions is introduced into a pump bottle. 3 grams of each composition are sprayed on a wig with 20 cm long hair shampooed and blotted beforehand. The wig is allowed to dry for 4 h and is turned upside down.

The wig is agitated by alternating rotation for 2 h. The final shape of the hair is compared with the shape that it had before the agitation, and the shape holding power is evaluated. Grades from 0 to 5 are used:

- 0 expresses a very poor shape holding power and an entirely collapsed hair style.
- 5 expresses an excellent holding power and a hair style that has remained intact and voluminous in spite of the agitation.

The wigs are then untangled and shaken again for 20 sec. The return of the shape of the hair style is evaluated when it has undergone all these operations. The same 0 to 5 grading grid is used.

Table 1 summarizes the results.

Table 1

/16

(1)		(2)
Composition	Tenue de la forme après agitation	Retour de la forme après agitation et démêlage
1	3,25	2,5
2	4,0	4,0
3	4,5	4,25
4	2,0	4,0
5	3,75	0,75
6	3,5	1,0
7	2,0	0,75
(3) sans traitement	0	0,5

Key: 1 Shape holding power after agitation  
 2 Return of the shape after agitation and untangling  
 3 Without treatment

Table 1 shows that the compositions according to the invention which contain the association of polymers provide better results in terms of shape holding power after agitation and return of the shape after agitation and untangling than the compositions according to prior art.

#### Example 2:

A composition 8 according to the invention is produced, and the hair style holding power as well as certain cosmetic properties are evaluated.

#### Composition 8 (invention):

AQ 1350	4g
Uramul SC 132	0.5 g
Water qs	100 g

A wig with 20 g of natural hair is taken, and 2.5 grams of composition 8 are applied on the hair and allowed to dry.

It is observed that the hair has a very good holding power. Untangling is easy, and the hair has a good feel after untangling.

#### Claims

/17

1. A cosmetic composition for keratinic fibers such as hair, characterized by the fact that it contains, in a cosmetically acceptable medium, at least one tacky polymer with a vitreous

transition temperature ( $T_g$ ) less than  $20^\circ\text{C}$  and at least one setting polymer with a vitreous transition temperature ( $T_g$ ) greater than  $15^\circ\text{C}$ :

2. A composition according to Claim 1, characterized by the fact that the tacky polymer has a detachment profile defined by a maximum detachment force of at least  $F_{\max} > 3$  Newton and preferably greater than 5 N.

3. A composition according to Claim 2, characterized by the fact that when the temperature of vitreous transition of the tacky polymer is less than  $-15^\circ\text{C}$ , the detachment profile is moreover defined by a separation energy  $S_{s(M/V)}$  of the material put in contact with a glass surface, which is less than  $300 \mu\text{J}$ .

4. A composition according to Claim 2, characterized by the fact that  $F_{\max}$  is the maximum tensile force, measured using an extensometer, necessary to detach the respective  $38 \text{ mm}^2$  surfaces of two rigid, inert, non-absorbent supports (A) and (B) placed facing one another; said surfaces being coated beforehand with the tacky polymer dissolved beforehand at a concentration of 5% in an aqueous, hydroalcoholic or alcoholic solvent, in a proportion of  $1 \text{ mg/mm}^2$ , dried for 24 h at  $22^\circ\text{C}$  in a relative humidity of 50%, and then subjected for 20 sec to a compression of 3 Newton, and finally subjected for 30 sec to traction at a speed of 20 mm/minute.

5. A composition according to Claim 4, characterized by the fact that supports (A) and (B) consist of polyethylene, polypropylene, metallic alloy or glass.

6. A composition according to Claim 2, characterized by the fact that  $S_{s(M/V)}$  is the energy provided by the extensometer in order to separate the respective  $38 \text{ mm}^2$  surfaces of two rigid, inert, non-absorbent supports (C) and (D) placed facing one another; one of said supports consisting of polished glass, and the nature of the other of said supports being identical to that of supports (A) and (B) as defined in Claim 4 or 5 and whose surface is coated beforehand with the tacky polymer dissolved beforehand at a concentration of 5% in an aqueous, hydroalcoholic or alcoholic solvent, in a proportion of  $1 \text{ mg/mm}^2$ , dried for 24 h at  $22^\circ\text{C}$  in a relative humidity of 50%, the two surfaces of said supports (C) and (D) being subjected for 20 sec to a compression of 3 Newton, and finally subjected for 30 sec to traction at a speed of 20 mm/minute.

/18

7. A composition according to Claim 6, characterized by the fact that  $S_{s(M/V)}$  is work which is computed by means of the following formula:

$$\int_{x_{s1} + 0,05}^{x_{s2}} F(x) dx$$

in which  $F(x)$  is the force necessary to produce a movement ( $x$ );

$x_{s1}$  is the movement (expressed in millimeters) produced by the maximum tensile force;  
 $X_{s2}$  in which [sic: is] the movement (expressed in millimeters) produced by the tensile force allowing complete separation of the two surfaces of supports (C) and (D).

8. A composition according to any one of the preceding claims, characterized by the fact that the tacky polymer is a branched sulfonic polyester or a (meth)-acrylic ester polymer [or] polymers.

9. A composition according to any one of the preceding claims, characterized by the fact that the relative concentration by weight of tacky polymer in the composition is greater than 0.01%, and preferably greater than 0.1%, and even more preferably greater than 0.5%.

10. A composition according to any one of the preceding claims, characterized by the fact that the setting polymer has a vitreous transition temperature ( $T_g$ ) greater than 25°C. /19

11. A composition according to any one of the preceding claims, characterized by the fact that the relative concentration by weight of setting polymer in the composition is greater than 0.01% and preferably greater than 0.1%.

12. A composition according to Claim 8, characterized by the fact that the branched sulfonic polyester is formed by polymerization of:

- (i) at least one bifunctional dicarboxylic acid carrying no sulfonic function;
- (ii) at least one bifunctional monomer carrying at least one sulfonic function, the functional group(s) being chosen from the group which includes the hydroxyl, carboxyl and amino groups;
- (iii) at least one diol or mixture of diol(s) and diamine(s);
- (iv) possibly, a bifunctional monomer chosen from the group which includes the carboxylic hydroxyacids, the carboxylic aminoacids and their mixtures;
- (v) at least one multifunctional reagent carrying at least three functional groups chosen from the group which includes the amino, alcohol and carboxylic acid groups.

13. A composition according to Claim 12, characterized by the fact that the polymerization is carried out using:

- (i) at least one bifunctional dicarboxylic acid carrying no sulfonic function;
- (ii) 2 to 15 relative mole % of bifunctional monomer carrying at least one sulfonic function;
- (iii) at least one diol or mixture of diol(s) and diamine(s);
- (iv) 0 to 40 relative mole % of the bifunctional monomer chosen from the group which includes the carboxylic hydroxyacids, the carboxylic aminoacids and their mixtures; /20
- (v) 0.1 to 40 relative mole % of the multifunctional reagent carrying at least three reactive functional groups.



14. A composition according to either of Claims 12 and 13, characterized by the fact that the branched sulfonic polymers contains substantially equal proportions, in number of equivalents, on one hand, of carboxylic acid functions, and on the other hand, of diol and/or diol and diamine functions.

15. A composition according to any one of Claims 12-14, characterized by the fact that the bifunctional dicarboxylic acid (i) is chosen from the group which includes the aliphatic dicarboxylic acids, the alicyclic dicarboxylic acids, the aromatic dicarboxylic acids.

16. A composition according to Claim 15, characterized by the fact that the bifunctional dicarboxylic acid (i) is chosen from the group which includes 1,4-cyclohexanediolic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, fumaric acid, maleic acid, 1,3-cyclohexanediolic acid, phthalic acid, terephthalic acid, and isophthalic acid and a mixture of them.

17. A composition according to any one of Claims 12-14, characterized by the fact that the bifunctional monomer (ii) is chosen from the group which includes the dicarboxylic acids, the dicarboxylic acid esters, the glycols and hydroxyacids each containing at least one sulfonate metal group.

18. A composition according to any one of Claims 12-14, characterized by the fact that the diol (iii) is chosen from the group which includes the alkanediols and the polyalkylenediols.

19. A composition according to Claim 18, characterized by the fact that the diol (iii) is chosen from the group which includes ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol and polypropylene glycol.

/21

20. A composition according to any one of Claims 12-14, characterized by the fact that the diamine (iii) is chosen from the group which includes the alkanediamines and the polyalkylenediamines.

21. A composition according to any one of Claims 12-14, characterized by the fact that the multifunctional reagent (v) is chosen from the group which includes trimethylolethane, trimethylolpropane, glycerol, pentaerythritol, sorbitol, trimellitic anhydride, erythritol, threitol, dipentaerythritol, pyromellitic dianhydride and dimethylpropionic acid.

22. A composition according to Claim 8, characterized by the fact that the (meth)-acrylic ester polymer advantageously includes:

- (a) 9 to 99 wt% of a (meth)-acrylic ester monomer with respect to the total weight of the polymer;
- (b) up to 90% co-monomer;
- (c) 1 to 10% of a vinylidene monomer containing a carboxyl or hydroxyl group.

23. A composition according to any one of the preceding claims, characterized by the fact that the setting polymer is chosen from the anionic, cationic, amphoteric, non-ionic setting polymers and their mixtures.

24. A composition according to Claim 23, characterized by the fact that the setting polymers are present in solubilized form or in the form of a dispersion of solid particles of polymer.

25. A composition according to Claim 24, characterized by the fact that the cationic setting polymers are chosen from the polymers containing primary, secondary, tertiary and/or quaternary amine groups which are part of the polymer chain or directly connected to it, and having a molecular weight between 500 and approximately 5,000,000 and preferably between 1,000 and 3,000,000. /22

26. A composition according to Claim 23, characterized by the fact that the anionic setting polymers are polymers containing groups derived from carboxylic, sulfonic or phosphoric acid and have a weight average molecular weight between 500 and 5,000,000.

27. A composition according to Claim 23, characterized by the fact that the amphoteric setting polymers are amphoteric polymers chosen from the polymers containing units B and C statistically distributed in the polymer chain, in which B designates a unit derived from a monomer containing at least one basic function, in particular a basic nitrogen atom, and C designates a unit derived from an acidic monomer containing one or more carboxylic or sulfonic groups, or else B and C can designate groups derived from zwitterionic monomers of carboxybetaines or sulfobetaines; B and C can also designate a cationic polymer chain containing primary, secondary, tertiary or quaternary amine groups, in which at least one of the amine groups carries a carboxylic or sulfonic group connected by the intermediary of a hydrocarbon radical; or else B and C are part of a chain of a polymer with an ethylene  $\alpha,\beta$ -dicarboxylic unit of which one of the carboxylic groups was reacted with a polyamine containing one or more primary or secondary amine groups.

28. A composition according to Claim 23, characterized by the fact that the non-ionic setting polymers are polyurethanes.

29. A composition according to Claim 1, characterized by the fact that the setting polymer is a hydrosoluble polymer chosen from the group which includes the acrylic polymers containing silicone, the polymers based on vinyl pyrrolidone and vinyl caprolactam monomer.

30. A composition according to Claim 1, characterized by the fact that the setting polymer is a dispersed polymer based on acrylic or methacrylic monomers and their esters and a polymer based on styrene monomers. /23

31. A composition according to any one of the preceding claims, characterized by the fact that it is present in the form of a spray composition, a foam, a gel or a lotion.

32. A composition according to any one of the preceding claims, characterized by the fact that the cosmetically acceptable vehicle consists of an appropriate solvent, to which additives can be added, such as gelling agents or foaming agents.

33. A composition according to any one of the preceding claims, characterized by the fact that it contains a solvent chosen from water, an alcohol or a hydroalcoholic mixture.

34. A composition according to any one of the preceding claims, characterized by the fact that it moreover contains an appropriate quantity of propellant made up of the usual compressed or liquefied gases, preferably compressed air, carbon dioxide or nitrogen, or else a gas which is soluble or not in the composition, such as dimethyl ether, the hydrocarbons containing or not containing fluorine, and their mixtures.

35. An aerosol device consisting of a vessel containing an aerosol composition made up, on one hand, of a liquid phase (or liquor) containing at least one composition according to any one of Claims 1 to 30 in an appropriate solvent and a propellant as well as a means for distribution of said aerosol composition.

36. A process for treatment of keratinic fibers, of hair in particular, characterized by the fact that the composition as defined in Claims 1-30 is applied on said fibers, before or after formation of the hair style.

/24

37. Use of a composition according to any one of Claims 1-30 in or for the manufacturing of a cosmetic hair styling formulation.

## INTERNATIONAL SEARCH REPORT

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 A61K7/06		International Application No PCT/FR 99/01347
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 A61K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 551 749 A (UNILEVER PLC ; UNILEVER NV (NL)) 21 July 1993 (1993-07-21) claims	1,8-37
A	US 5 441 728 A (TSAUR LIANG S ET AL) 15 August 1995 (1995-08-15) claims	1,8-11, 22-37
A	US 5 266 303 A (MYERS GARRY L ET AL) 30 November 1993 (1993-11-30) claims	1,8-19, 31-37
A	WO 95 00105 A (EASTMAN CHEM CO) 5 January 1995 (1995-01-05) the whole document	1,8-19, 31-37
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Δ" document member of the same patent family		
Date of the actual completion of the international search:  1 October 1999		Date of mailing of the international search report  11/10/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016		Authorized officer  Couckuyt, P

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/FR 99/01347

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 524 346 A (CURTIS HELENE IND INC) 27 January 1993 (1993-01-27) claims	1,8-19, 31-37
A	WO 95 33437 A (EASTMAN CHEM CO) 14 December 1995 (1995-12-14) claims	1,8-19, 31-37

## - INTERNATIONAL SEARCH REPORT

International application No.

PCT/FR 99/ 01347

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 2-7  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
  
See supplementary sheet INFORMATION FOLLOW-UP PCT/ISA/210
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/FR 99/01347

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0551749 A	21-07-1993	AT 156697 T	15-08-1997
		AU 652303 B	18-08-1994
		AU 3030092 A	24-06-1993
		BR 9205094 A	22-06-1993
		CA 2085641 A,C	21-06-1993
		DE 69221600 D	18-09-1997
		DE 69221600 T	18-12-1997
		ES 2104859 T	16-10-1997
		JP 2571744 B	16-01-1997
		JP 5255050 A	05-10-1993
		KR 9616191 B	06-12-1996
		US 5840292 A	24-11-1998
		ZA 9209853 A	20-06-1994
US 5441728 A	15-08-1995	CA 2152296 A	23-12-1995
		EP 0688557 A	27-12-1995
US 5266303 A	30-11-1993	AT 176755 T	15-03-1999
		CA 2149425 A,C	09-06-1994
		DE 69323557 D	25-03-1999
		DE 69323557 T	17-06-1999
		EP 0670710 A	13-09-1995
		JP 8503943 T	30-04-1996
		MX 9306955 A	31-01-1995
		WO 9412148 A	09-06-1994
WO 9500105 A	05-01-1995	AU 671924 B	12-09-1996
		AU 7172094 A	17-01-1995
		CA 2165991 A	05-01-1995
		DE 69405745 D	23-10-1997
		DE 69405745 T	08-01-1998
		EP 0705093 A	10-04-1996
		JP 8511803 T	10-12-1996
		US 5662893 A	02-09-1997
		US 5674479 A	07-10-1997
		US 5660816 A	26-08-1997
		US 5853701 A	29-12-1998
EP 0524346 A	27-01-1993	AT 167391 T	15-07-1998
		AU 652008 B	11-08-1994
		AU 8968191 A	28-01-1993
		CA 2057607 A,C	24-01-1993
		DE 69129624 D	23-07-1998
		DE 69129624 T	07-01-1999
		ES 2119754 T	16-10-1998
		FI 915889 A	24-01-1993
		JP 6009343 A	18-01-1994
		MX 9102554 A	01-01-1993
		US 5639448 A	17-06-1997
WO 9533437 A	14-12-1995	US 5674479 A	07-10-1997
		AU 2594295 A	04-01-1996
		CA 2190746 A	14-12-1995
		CN 1149825 A	14-05-1997
		EP 0762866 A	19-03-1997
		JP 10501227 T	03-02-1998
		US 5853701 A	29-12-1998